DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the nonaqueous electrolyte secondary battery using nonaqueous electrolyte and this excellent in battery characteristics, such as generation-of-gas control at the time of the high temperature preservation of a cell and/or a cycle characteristic, electric capacity, and a conservation characteristic.
[0002]
[Description of the Prior Art]In recent years, portable-izing of consumer electronics and cordless making are progressing quickly. The requests to the rechargeable battery which has the small size, light weight, and thin shape which bear the power supply for a drive along with this, and has high energy density are mounting. In it, the rechargeable battery using nonaqueous electrolyte especially a rechargeable lithium-ion battery, and a lithium polymer secondary battery especially have high tension and high energy density, and promising ** is carried out as a cell which can be slimmed down, and the development is performed briskly.
[0003]There is a thing using occlusion, and metallic compounds and the carbon material which can be emitted as a charge of a principal member in the negative electrode of these nonaqueous electrolyte secondary batteries by charge and discharge about what uses metal lithium itself as an active material, and lithium of an active material. among these -- the present -- many cases -- a carbon material -- as negative electrode active material -- business -- ******** .
[0004]Usually, a protective film is formed in the surface of the negative electrode using a carbon material by the reaction of an electrolysis solution and a negative electrode, and the chemical stability of the negative electrode is maintained by the protective film. However, when a cell was saved at an elevated temperature, the crack went into said protective film easily, and the technical problem that the nonaqueous solvent in an electrolysis solution reacted to a

negative electrode, and the generation of gas was carried out in the crack portion occurred. The technical problem in which a carbon material exfoliates easily from a negative electrode at the time of charge of a cell occurred. In the interface of the carbon material in a negative electrode, and nonaqueous electrolyte, the reaction to which a nonaqueous solvent is returned electrochemically occurs, and this is considered for the gas emitted in that case to exert a physical operation on a carbon material.

[0005]Various kinds of lithium content multiple oxides in which the occlusion and discharge of lithium by charge and discharge are possible are generally used for the anode of the nonaqueous electrolyte secondary battery as an active material. In the nonaqueous electrolyte secondary battery provided with these anodes and carbon negative electrodes, when the binder of positive and negative poles swelled with an electrolysis solution during a charging and discharging cycle and preservation, the impedance of the electrode rose and the technical problem that cell capacity fell gradually occurred.

[0006]In particular, in a lithium polymer secondary battery, many saccate armor bodies which consist of a laminate sheet which arranged and laminated the metallic foil between resin films instead of the metal casing used with the rechargeable lithium-ion battery for small size, a light weight, and slimming down are used. In that case, even when few quantity of gas was emitted by disassembly of the nonaqueous solvent in the time of the high temperature preservation of a cell, etc., the important technical problem that it had adverse effects, such as an increase in cell thickness, a liquid spill, and charge-and-discharge characteristic degradation, occurred by the rise of inter cell pressure.

[0007]

[Problem(s) to be Solved by the Invention]This invention solves the technical problem about the electrolysis solution of such a nonaqueous electrolyte secondary battery, and an object of this invention is to provide the nonaqueous electrolyte secondary battery using nonaqueous electrolyte and this excellent also in battery characteristics, such as generation-of-gas control at the time of high temperature preservation and/or a cycle characteristic, cell capacity, and a conservation characteristic.

[0008]

[Means for Solving the Problem]Nonaqueous electrolyte of this invention for attaining the above-mentioned purpose, It is a thing, wherein it consists of a solute which dissolved in a nonaqueous solvent and said nonaqueous solvent and said nonaqueous solvent contains propylene carbonate (PC) and a 1,3-propane sultone (PS), It is preferred that content whose content of PC is 0.1 % of the weight - 5.0 % of the weight, and PS is 0.1 % of the weight - 6.5 % of the weight.

[0009]Nonaqueous electrolyte of this invention consists of a nonaqueous solvent and a solute which was alike and dissolved in said nonaqueous solvent, and said nonaqueous solvent

Vinylene carbonate (VC), At least one kind chosen from diphenyldisulfide (DPDS), di-p-tolyl disulfide (DTDS), and bis(4-methoxypheny)disulfide (BMPDS) is contained.
[0010]At least one kind which it consisted of a nonaqueous solvent and a solute which was alike and dissolved in said nonaqueous solvent, and PC and PS contained in said nonaqueous solvent, and was chosen from VC, DPDS, DTDS, and BMPDS contains nonaqueous electrolyte of this invention.
[0011]Content of PC and PS which one in above-mentioned this invention of nonaqueous solvents contains, and VC, It is preferred that they are 0.1 to 5.0 % of the weight, 0.1 to 6.5 % of the weight, and 0.1 to 5.0 % of the weight, respectively, and, as for at least one kind of content chosen from DPDS, DTDS, and BMPDS, it is preferred that they are 0.1 % of the weight - 0.6 % of the weight in a total amount.
[0012]Nonaqueous electrolyte of this invention consists of a solute which dissolved in a nonaqueous solvent and said nonaqueous solvent, It is characterized by said nonaqueous solvent containing at least one kind further chosen from DPDS, DTDS, and BMPDS including PC, PS, and VC, and it is preferred that the sum totals of such content are 0.4 % of the weight - 17.1 % of the weight.
[0013]Each nonaqueous electrolyte of above-mentioned this invention was used for a nonaqueous electrolyte secondary battery of this invention as an electrolysis solution.
[0014]
[Embodiment of the Invention]As for the nonaqueous solvent in the nonaqueous electrolyte of this invention, it is preferred to contain cyclic carbonate and chain carbonate as the main ingredients. It is preferred that it is at least one kind chosen from ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC) as said cyclic carbonate.
[0015]It is preferred that it is at least one kind chosen from dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) as said chain carbonate.
[0016]In the nonaqueous electrolyte in this invention, the content of cyclic carbonate in said nonaqueous solvent is 10 % of the weight - 70 % of the weight, and it is preferred that the content of said chain carbonate is 30 % of the weight - 90 % of the weight.
[0017]As a solute which can be used by this invention, $LiClO_4$, $LiBF_4$, $LiPF_6$, $LiAlCl_4$, $LiSbF_6$, LiSCN, LiCl, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiN(C_2F_5SO_2)_2$, $LiAsF_6$, There are $LiN(CF_3SO_2)_2$ and $Li_2B_{10}Cl_{10}$, low-grade aliphatic-carboxylic-acid lithium, LiBr, LiI, chloroboranelithium, 4 phenyl lithium borate, and imide. These can be used as a solute combining independent or two kinds or more. Especially the thing for which a $LiPF_6$ independent or this is used as a solute combining other lithium salt also in these is preferred.
[0018]After the nonaqueous electrolyte of this invention dissolves the aforementioned solute in the nonaqueous solvent which mixed cyclic carbonate and chain carbonate of the main

ingredients by the concentration of 0.5-1.5M, for example, it is preferred to prepare by dissolving said additive agent.

[0019]in addition -- this invention -- the content of each nonaqueous solvent in nonaqueous electrolyte -- respectively -- weight % -- a table -- the bottom of this weight % is the weight percent of each nonaqueous solvent at the time of making the weight sum of all the nonaqueous solvents in nonaqueous electrolyte into 100%.

[0020]It is not limited in particular for members forming or materials other than the electrolysis solution which constitutes a nonaqueous electrolyte secondary battery, but what is used from the former can be used. For example, as positive active material, discharge and the lithium containing compound metal oxide which can carry out occlusion can be used for a lithium ion by charge and discharge. As a lithium containing compound metal oxide, Li_xCoO_2, Li_xNiO_2, Li_xMnO_2, Li_xCo_ynickel$_{1-y}O_2$, $Li_xCo_yM_{1-y}O_z$, Li_xnickel$_{1-y}M_yO_z$, $Li_xMn_2O_4$, $Li_xMn_{2-y}M_yO_4$ (here) At least one kind in M=Na, Mg, Sc, Y, Mn, Fe, Co, nickel, Cu, Zn, aluminum, Cr, Pb, Sb, and B, x= 0-1.2, y= 0 to 0.9, z= 2.0-2.3, etc. are mentioned. The above-mentioned x value is a value before a charge-and-discharge start, and is fluctuated by charge and discharge.

[0021]It is also possible to use a transition metal chalcogen ghost, the lithium compound of a vanadium oxide, and the lithium compound of a niobium oxidation thing besides the above. It is also possible to mix and use combining the above-mentioned positive electrode material. As for the mean particle diameter of positive active material, although limitation in particular is not carried out, it is preferred that they are 1 micrometer - 30 micrometers.

[0022]It is preferred to use the material, for example, natural graphite, containing the graphite which can use occlusion and the carbon material which can be emitted for a lithium ion, and has a graphite mold crystal structure especially by charge and discharge, and an artificial graphite as negative electrode active material. It is much more preferred that the spacing (d_{002}) of a lattice plane (002) uses especially the graphite which is 3.350-3.400 A.

[0023]As a binder for maintaining the adhesion between an anode or negative electrode active material, The copolymer (P (VDF-HFP)) of fluororesin material (PVDF), for example, polyvinylidene fluoride, vinylidene fluoride, and hexafluoropropylene, Or it is preferred to mix and use either of the polytetrafluoroethylenes (PTFE) or these two kinds or more.

[0024]In this invention, PC and PS which are contained in the nonaqueous solvent in nonaqueous electrolyte contribute to formation of the stable protective film on the surface of a negative electrode carbon material. This protective film is a stable film which a crack does not generate in the time of the high temperature preservation of a cell, either. Even when the carbon material high-crystallized in the activity of natural graphite, an artificial graphite, etc. by covering a carbon negative electrode with said protective film is used for a negative electrode, the effect which disassembly of the nonaqueous solvent in the electrolysis solution in the time

of high temperature preservation is controlled, and controls the generation of gas is demonstrated. And this protective film does not bar the normal reaction of the charge and discharge of a cell.

[0025]VC, DPDS, DPTS, and BMPDS which are added to nonaqueous electrolyte contribute to stable protective film formation in the negative electrode carbon material surface. As for this protective film, a stable state is maintained also in a repetition of charge and discharge. The nonaqueous solvent in an electrolysis solution being returned electrochemically, and carrying out the generation of gas by operation of this protective film, is controlled. As a result, the exfoliation from the negative electrode of a negative electrode carbon material can be controlled, and a cycle characteristic can be raised. And this protective film does not bar the normal charge-and-discharge reaction of a cell.

[0026]The resultant of the nonaqueous solvent at the time of said protective film formation and a carbon negative electrode acts on the polar group end which exists in PVDF which is a binder, P (VDF-HFP), etc., DPDS, DTDS, and BMPDS control swelling of the binder by a nonaqueous solvent, and the adhesion between electrode materials is maintained. Thereby, an impedance rise of an electrode is controlled and it is thought that the effect of raising a cycle characteristic further is demonstrated.

[0027]As a separator used for this invention, the big degree of ion permeation, a predetermined mechanical strength, and the porous film that consists of polymer which carries out absorption maintenance of the fine porous thin film provided with insulation or the nonaqueous electrolyte are used. The sheet, the nonwoven fabric, or textile fabrics made from olefin system polymer or glass fibers etc. which were independent or combined these, such as polypropylene from organic solvent-proof nature and hydrophobicity and polyethylene, can also be used as a separator.

[0028]As for the aperture of a separator, it is preferred that it is a size of the range which the active material of the positive and negative poles from which it was desorbed from the positive-and-negative-poles board, a binder, or a conducting agent does not penetrate, for example, what is 0.01 micrometer - 1 micrometer is preferred. In order to secure the safety at the time of a short circuit, a thing with the function to fuse above constant temperature, to blockade a hole and to increase resistance is preferred. As for the thickness of a separator, generally, a thing (10 micrometers - 300 micrometers) is used. Although a void content is determined according to the permeability of ion, the kind of raw material, or thickness, it is preferred that it is generally 30 to 80%.

[0029]It is also preferred to include what carried out absorption maintenance of the nonaqueous electrolyte which dissolved lithium salt in the polymeric material at the organic solvent in positive electrode mixture and/or negative electrode mixture, to unite with an anode and a negative electrode the porous separator which consists of polymer which carries out

absorption maintenance of the nonaqueous electrolyte further, and to constitute a cell. As this polymeric material, be [what is necessary / just although the absorption maintenance of the nonaqueous electrolyte can be carried out], especially the copolymer of vinylidene fluoride and hexafluoropropylene is preferred.

[0030]The shape of this invention is applicable to the large-sized thing etc. which are used for a coin type, a button type, a sheet type, a lamination type, cylindrical, flat, a square shape, an electromobile, etc.

[0031]The nonaqueous electrolyte secondary battery of this invention can be used for a Personal Digital Assistant, a portable electronic apparatus, a home small stationary energy storage apparatus, a motor bicycle, an electromobile, a hybrid electric vehicle, etc., and is not limited to these uses in particular.

[0032]

[Example]Hereafter, an example and a comparative example are given and the details of this invention are explained.

[0033]Drawing 1 is a front view of the lithium-polymer battery produced in each example and each comparative example of this invention, and drawing 2 is a sectional view of the A-B section. Hereafter, the anode board, the negative electrode plate and the manufacturing method of a battery element common to the cell in each example and each comparative example, and the constitution method of a cell are explained using drawing 1 and drawing 2.

[0034]1. The paste to which kneading dispersion of $LiCoO_2$ as manufacturing method positive active material of an anode board, acetylene black as a conducting agent, and the polymer (P (VDF-HFP)) as a binder and electrolysis solution hold-back agent was carried out with the organic solvent which consists of N-methyl-2-pyrrolidone (NMP) was prepared. The anode board 1 was produced by plastering with aluminium foil the positive pole collector 1a which carried out Russ processing, drying and rolling this paste, and forming the positive electrode mixture layer 1b.

[0035]2. The paste to which kneading dispersion of the artificial graphite (d_{002}=3.355A) which is the manufacturing method negative electrode active material of a negative electrode plate, and the powder of P (VDF-HFP) was carried out by NMP was prepared. The negative electrode plate 2 was produced by drying and rolling [plaster and] this paste to both sides of the charge collector 2a which carried out Russ processing of the copper foil, and forming negative electrode mixture layer 2b.

[0036]3. production of a battery element -- inserting the separator 3 made from polymer which consists of a film of said P (VDF-HFP) between the two anode boards 1 produced as mentioned above, inserting the negative electrode plate 2 between this separator 3, and, Heating these to a fixed temperature, it pressurized and the battery element 4 by which laminate integration was carried out was constituted.

[0037]4. As shown in constitution method drawing 1 and drawing 2 of a cell, the piece 5 of a positive electrode lead made from aluminium foil was welded to the lead piece mounting part 1c of the positive pole collector 1a, and the piece 6 made from copper foil of a negative electrode lead was further welded to the lead piece mounting part 2c of the negative pole collector 2a. 7 -- aluminium foil -- middle -- much more -- it is the saccate armor body formed from the laminate film which carried out, united the polypropylene film with the inside and unified the polyethylene terephthalate film and the nylon film outside, respectively. The piece 5 of a positive electrode lead and the piece 6 of a negative electrode lead were pulled out to the exterior of the saccate armor body among the battery elements 4 accommodated in the inside of this saccate armor body 7, and those tip parts were made into in-and-out power terminal 5a ** 6a of positive and negative poles, respectively.
[0038]When 8 and 9 carry out hot welding of the opening of the saccate armor body 7, they are the protective films for securing the lead piece 5 or 6 and the electric insulation between laminate films, and airtightness. The saccate armor body 7 cut the aforementioned laminate film to band-like, folded and carried out it in the two center section of the length direction, and thermal melting arrival carried out two sides of the cross direction beforehand, and it produced them. 7a is a heat sealed part of said transverse direction. After inserting the battery element 4 from the opening of the saccate armor body 7 and pouring in a predetermined electrolysis solution, said opening was sealed by thermal melting arrival. 7b is the heat welding. Thus, the nominal capacity 500mAh lithium-polymer battery was produced.
[0039]The adjustment method of each nonaqueous electrolyte used for the lithium-polymer battery produced by each example and each comparative example is shown below.
[0040](Example 1) The weight ratio of EC, and EMC and DEC dissolved $LiPF_6$ of 1.35M as a solute, carried out addition mixing of 2.0 more% of the weight of PC, and 4.0% of the weight of the PS, and adjusted nonaqueous electrolyte to the mixed solvent which is 4:5:2.
[0041](Comparative example 1) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1.
[0042](Comparative example 2) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 6.0 more% of the weight of the PC was carried out, and nonaqueous electrolyte was adjusted.
[0043](Comparative example 3) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 6.0 more% of the weight of the PS was carried out, and nonaqueous electrolyte was adjusted.
[0044](Example 2) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of VC and 0.1% of the weight of the DPDS was carried out, and nonaqueous electrolyte was adjusted.
[0045](Example 3) The same solute as Example 1 was dissolved in the same mixed solvent as

Example 1, addition mixing of 0.5 more% of the weight of VC and 0.1% of the weight of the DTDS was carried out, and nonaqueous electrolyte was adjusted.

[0046](Example 4) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of VC and 0.1% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0047](Example 5) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC and 0.4% of the weight of the DPDS was carried out, and nonaqueous electrolyte was adjusted.

[0048](Example 6) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC and 0.4% of the weight of the DTDS was carried out, and nonaqueous electrolyte was adjusted.

[0049](Example 7) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC and 0.4% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0050](Example 8) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of VC, 0.1% of the weight of DPDS, and 0.1% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0051](Example 9) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of VC, 0.1% of the weight of DTDS, and the 0.1-% of the weight BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0052](Example 10) dissolving the same solute as Example 1 in the same mixed solvent as Example 1 -- 0.5 more% of the weight of VC, and 0.1 % of the weight -- DPDS(ing) and 0.1-% of the weight DTDS addition mixing were carried out, and nonaqueous electrolyte was adjusted.

[0053](Example 11) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC, 0.2% of the weight of DPDS, and the 0.4-% of the weight DTDS was carried out, and nonaqueous electrolyte was adjusted.

[0054](Example 12) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC, 0.2% of the weight of DPDS, and 0.4% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0055](Example 13) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC, 0.4% of the weight of DTDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0056](Example 14) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of VC, 0.1% of the weight of DPDS, 0.1% of the weight of DTDS, and 0.1% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.
[0057](Example 15) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 3.0 more% of the weight of VC, 0.2% of the weight of DPDS, 0.2% of the weight of DTDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.
[0058](Comparative example 4) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of the VC was carried out, and nonaqueous electrolyte was adjusted.
[0059](Comparative example 5) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 0.5 more% of the weight of the DPDS was carried out, and nonaqueous electrolyte was adjusted.
[0060](Example 16) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, and 0.5% of the weight of the VC was carried out, and nonaqueous electrolyte was adjusted.
[0061](Example 17) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, and 0.2% of the weight of the DPDS was carried out, and nonaqueous electrolyte was adjusted.
[0062](Example 18) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, and 0.2% of the weight of the DTDS was carried out, and nonaqueous electrolyte was adjusted.
[0063](Example 19) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.
[0064](Example 20) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, and 0.2% of the weight of the DPDS was carried out, and nonaqueous electrolyte was adjusted.
[0065](Example 21) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, and 0.2% of the weight of the DTDS was carried out, and nonaqueous electrolyte was adjusted.
[0066](Example 22) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, and 0.2% of the weight of the BMPDS was carried out, and

nonaqueous electrolyte was adjusted.

[0067](Example 23) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.2% of the weight of DPDS, and 0.2% of the weight of the DTDS was carried out, and nonaqueous electrolyte was adjusted.

[0068](Example 24) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.2% of the weight of DPDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0069](Example 25) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.2% of the weight of DTDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0070](Example 26) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, 0.2% of the weight of DPDS, and 0.2% of the weight of the DTDS was carried out, and nonaqueous electrolyte was adjusted.

[0071](Example 27) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, 0.2% of the weight of DPDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0072](Example 28) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, 0.2% of the weight of DTDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0073](Example 29) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.2% of the weight of DPDS, 0.2% of the weight of DTDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0074](Example 30) The same solute as Example 1 was dissolved in the same mixed solvent as Example 1, addition mixing of 2.0 more% of the weight of PC, 4.0% of the weight of PS, 0.8% of the weight of VC, 0.2% of the weight of DPDS, 0.2% of the weight of DTDS, and 0.2% of the weight of the BMPDS was carried out, and nonaqueous electrolyte was adjusted.

[0075](a. High-temperature-preservation examination) The high-temperature-preservation examination was done about each lithium-polymer battery produced by Example 1 - Example 30 and the comparative example 1 - the comparative example 3. First, it charged until cell voltage was set to 4.2V by 300 mA (0.6C) charging current in a 25 ** thermostat, further, it

charged until charging current was set to 50 mA (0.1C) with the constant voltage of 4.2V, and charge was completed. Thus, the result of having measured cell thickness for the cell which completed charge in the thermostat 90 ** thermostat ON ** and 4 hours afterward is shown in Table 1, 2, and 3. PC, PS, VC, DPDS, DTDS, and BMPDS show propylene carbonate, a 1,3-propane sultone, vinylene carbonate, diphenyldisulfide, di-p-tolyl disulfide, and bis(4-methoxypheny)disulfide among front, respectively.

[0076](b. Cycle characteristic) The charge-and-discharge cycle test was done about each lithium-polymer battery produced by Examples 2-15 and the comparative example 1. First, after completing charge by the same method as the case of said high-temperature-preservation examination, final voltage repeated the charging and discharging cycle discharged to 3.0V by the GSM pulse discharge (it is a pulse discharge with discharge of 4msec. at discharge of 0.6 sec., and 150 mA in 1700 mA) of 352 mA of average current. The result of having measured the service capacity maintenance factor after 100 cycles when initial service capacity is made into 100% is shown in Table 2 and 3.

[0077]

[Table 1]

	非水溶媒中の含有量 PC／PS 重量%	電池厚みの増加 90℃−4h後 mm
実施例1	2. 0／4. 0	0. 241
比較例1	0. 0／0. 0	1. 160
比較例2	6. 0／0. 0	0. 350
比較例3	0. 0／6. 0	0. 308

[0078]

[Table 2]

	非水溶媒中の含有量 VC/DPDS/DTDS/BMPDS 重量%	電池厚みの増加 90℃−4h後 mm	サイクル特性 100サイクル後 %
実施例2	0. 5／0. 1／0. 0／0. 0	1. 26	91. 1
実施例3	0. 5／0. 0／0. 1／0. 0	1. 22	90. 7
実施例4	0. 5／0. 0／0. 0／0. 1	1. 25	91. 2
実施例5	3. 0／0. 4／0. 0／0. 0	1. 21	91. 3
実施例6	3. 0／0. 0／0. 4／0. 0	1. 20	90. 3
実施例7	3. 0／0. 0／0. 0／0. 4	1. 19	91. 0
実施例8	0. 5／0. 1／0. 0／0. 1	1. 18	89. 9
実施例9	0. 5／0. 0／0. 1／0. 1	1. 24	90. 8
実施例10	0. 5／0. 1／0. 1／0. 0	1. 25	90. 3
実施例11	3. 0／0. 2／0. 4／0. 0	1. 26	91. 4
実施例12	3. 0／0. 2／0. 0／0. 4	1. 25	91. 0
実施例13	3. 0／0. 0／0. 4／0. 2	1. 20	91. 2
実施例14	0. 5／0. 1／0. 1／0. 1	1. 21	89. 9
実施例15	3. 0／0. 2／0. 2／0. 2	1. 22	91. 3
比較例1	0. 0／0. 0／0. 0／0. 0	1. 16	79. 7
比較例4	0. 5／0. 0／0. 0／0. 0	1. 22	84. 8
比較例5	0. 0／0. 5／0. 0／0. 0	1. 23	83. 9

[0079]

[Table 3]

	非水溶媒中の含有量 PC/PS/VC/DPDS/DTDS/BMPDS 重量%	電池厚みの増加 90℃−4h後 mm	サイクル特性 100サイクル後 %
実施例16	2. 0/4. 0/0. 5/0. 0/0. 0/0. 0	0. 241	89. 9
実施例17	2. 0/4. 0/0. 0/0. 2/0. 0/0. 0	0. 212	88. 5
実施例18	2. 0/4. 0/0. 0/0. 0/0. 2/0. 0	0. 203	89. 5
実施例19	2. 0/4. 0/0. 0/0. 0/0. 0/0. 2	0. 213	88. 9
実施例20	2. 0/4. 0/0. 8/0. 2/0. 0/0. 0	0. 253	93. 2
実施例21	2. 0/4. 0/0. 8/0. 0/0. 2/0. 0	0. 243	93. 0
実施例22	2. 0/4. 0/0. 8/0. 0/0. 0/0. 2	0. 205	93. 8
実施例23	2. 0/4. 0/0. 0/0. 2/0. 2/0. 0	0. 206	89. 2
実施例24	2. 0/4. 0/0. 0/0. 2/0. 0/0. 2	0. 241	89. 4
実施例25	2. 0/4. 0/0. 0/0. 0/0. 2/0. 2	0. 211	89. 6
実施例26	2. 0/4. 0/0. 8/0. 2/0. 2/0. 0	0. 252	94. 2
実施例27	2. 0/4. 0/0. 8/0. 2/0. 0/0. 2	0. 232	94. 6
実施例28	2. 0/4. 0/0. 8/0. 0/0. 2/0. 2	0. 241	95. 0
実施例29	2. 0/4. 0/0. 0/0. 2/0. 2/0. 2	0. 221	89. 4
実施例30	2. 0/4. 0/0. 8/0. 2/0. 2/0. 2	0. 218	94. 2
比較例1	0. 0/0. 0/0. 0/0. 0/0. 0/0. 0	1. 160	79. 7

[0080]The comparative example 1 could not control the generating gas at the time of 90 ** preservation, but the increase in the cell thickness after the high temperature preservation 4h showed the value as big as 1.160 mm so that clearly from Table 1. On the other hand, Example 1 shows the outstanding generation-of-gas depressor effect as compared with the comparative example 3 which added only the comparative example 2 which added only PC, and PS.
The remarkable synergistic effect by using PC and PS together from these results has been checked.

[0081]The capacity maintenance rate after 100 cycles of the comparative example 1 was 79.7% so that clearly from Table 2. On the other hand, Example 2 - Example 15 have a capacity maintenance rate of 89 to 91%, and it compares with the comparative example 4 which added only VC, and the comparative example 5 which added only DPDS, All are excellent in the cycle characteristic and the synergistic effect outstanding as a cycle characteristic improvement additive agent has been checked by adding at least one kind chosen from VC, DPDS, DTDS, and BMPDS from these results.
[0082]However, in the cell of Example 2 - Example 15, although it was small, cell thickness increased, these additive agents decomposed at the time of an elevated temperature, and the action which carries out the generation of gas was suggested. The increase in the gas yield by this comes out only, like a cylindrical shape lithium secondary battery, in a nonaqueous electrolyte secondary battery with large case strength, there is no technical problem of cell thickness increasing, and, for a certain reason, an effect can fully be demonstrated.
[0083]As for the comparative example 1, the increase in cell thickness of the capacity maintenance rate after 1.160 mm and 100 cycles was 79.7% so that clearly from Table 3. On the other hand, the cell of Example 16 - Example 30 has checked the effect from which the capacity maintenance rate after 0.20-0.26 mm and 100 cycles is 88 to 95% and which all

excelled [increase / in cell thickness] in the generation-of-gas depressor effect at the time of high temperature preservation, and the improvement in a cycle characteristic.

[0084]It turned out that VC, DPDS, DTDS, and BMPDS which are the additive agents which excelled the above result in the effect of raising a cycle characteristic control the hot generation of gas by using together with PC and PS, respectively, and a cycle characteristic is raised. Especially when at least one kind especially chosen from PC, PS, VC, DPDS and DTDS, and BMPDS was added, it turned out that the outstanding effect is acquired.

[0085]JP,10-247517,A has the indication which raises the safety at the time of overcharge by adding DPDS to an electrolysis solution. However, when DPDS was added in the electrolysis solution at 3% of high concentration currently indicated in the example, the safety at the time of overcharge improved, but the hot generation of gas is remarkable and the technical problem of the generation of gas was not able to be solved. By pressing down the content of DPDS in a solvent in a minute amount very much like this invention with 0.1 % of the weight - 0.6 % of the weight, and making PC and PS use together, the hot generation of gas was able to be controlled and the cycle characteristic was able to be raised.

[0086]Although it is proposed that the cycle characteristic of a cell and a conservation characteristic improve by adding di-p-tolyl disulfide to an electrolysis solution at JP,2000-149986,A, Only now, the problem of cell bulging at the time of high temperature preservation could not be solved, the hot generation of gas was able to be controlled by using PC and PS together like this invention, and the cycle characteristic was able to be raised.

[0087]Although the example which mixes PC, chain carbonate, and VC is indicated by JP,11-67266,A, The addition of VC was able to be added in 0.1 to 5.0%, and a minute amount like this invention, and the hot generation of gas was able to be controlled by using PC and PS together, and the cycle characteristic was able to be raised.

[0088]5. Nonaqueous electrolyte was adjusted like Example 16 except having made the addition of PS into 0.1 % of the weight for the examination (example 31) PC addition of the content of the additive agent in a nonaqueous solvent 0.1% of the weight.

[0089](Example 32) Nonaqueous electrolyte was adjusted like Example 16 except having made the addition of PS into 6.5 % of the weight for the addition of PC 5.0% of the weight.

[0090](Example 33) Nonaqueous electrolyte was adjusted like Example 16 except having made the addition of VC into 0.1 % of the weight.

[0091](Example 34) Nonaqueous electrolyte was adjusted like Example 16 except having made the addition of VC into 1.0 % of the weight.

[0092](Example 35) Nonaqueous electrolyte was adjusted like Example 20 except having made the addition of VC into 5.0 % of the weight.

[0093](Example 36) Nonaqueous electrolyte was adjusted like Example 20 except having made the addition of DPDS into 0.1 % of the weight.

[0094](Example 37) Nonaqueous electrolyte was adjusted like Example 20 except having made the addition of DPDS into 0.4 % of the weight.
[0095](Example 38) Nonaqueous electrolyte was adjusted like Example 20 except having made the addition of DPDS into 0.6 % of the weight.
[0096](Example 39) Nonaqueous electrolyte was adjusted like Example 21 except having made the addition of DTDS into 0.1 % of the weight.
[0097](Example 40) Nonaqueous electrolyte was adjusted like Example 21 except having made the addition of DTDS into 0.6 % of the weight.
[0098](Example 41) Nonaqueous electrolyte was adjusted like Example 22 except having made the addition of BMPDS into 0.1 % of the weight.
[0099](Example 42) Nonaqueous electrolyte was adjusted like Example 22 except having made the addition of BMPDS into 0.6 % of the weight.
[0100](Example 43) Nonaqueous electrolyte was adjusted like Example 20 except having made the addition of PC, PS, VC, and DPDS into 0.1 % of the weight, respectively.
[0101](Example 44) Nonaqueous electrolyte was adjusted like Example 20 except having made the addition of PC, PS, VC, and DPDS into 5.0 % of the weight, 6.5 % of the weight, 5.0 % of the weight, and 0.6 % of the weight, respectively.
[0102](Example 45) Nonaqueous electrolyte was adjusted like Example 21 except having made the addition of PC, PS, VC, and DTDS into 0.1 % of the weight, respectively.
[0103](Example 46) Nonaqueous electrolyte was adjusted like Example 21 except having made the addition of PC, PS, VC, and DTDS into 5.0 % of the weight, 6.5 % of the weight, 5.0 % of the weight, and 0.6 % of the weight, respectively.
[0104](Example 47) Nonaqueous electrolyte was adjusted like Example 22 except having made the addition of PC, PS, VC, and BMPDS into 0.1 % of the weight, respectively.
[0105](Example 48) Nonaqueous electrolyte was adjusted like Example 22 except having made the addition of PC, PS, VC, and BMPDS into 5.0 % of the weight, 6.5 % of the weight, 5.0 % of the weight, and 0.6 % of the weight, respectively.
[0106]Thus, about the lithium-polymer battery produced in Example 31 - Example 48, the high-temperature-preservation examination was done in the similar way with having examined about each cell of Example 1 - Example 30 and the comparative example 1 - the comparative example 3. The charge-and-discharge cycle test was done in the similar way about each cell of the above-mentioned Example 31 - Example 48 with having examined about each cell of Example 2 - Example 15, and the comparative example 1. These results are shown in Table 4.

[0107]
[Table 4]

	非水溶媒中の含有量 PC/PS/VC/DPDS/DTDS/BMPDS 重量%	電池厚みの増加 90℃−4h後 mm	サイクル特性 100サイクル後 %
実施例31	0. 1／0. 1／0. 5／0. 0／0. 0／0. 0	0. 198	89. 3
実施例32	5. 0／6. 5／0. 5／0. 0／0. 0／0. 0	0. 201	89. 2
実施例33	2. 0／4. 0／0. 1／0. 0／0. 0／0. 0	0. 239	88. 1
実施例34	2. 0／4. 0／1. 0／0. 0／0. 0／0. 0	0. 230	90. 3
実施例35	2. 0／4. 0／5. 0／0. 2／0. 0／0. 0	0. 203	93. 2
実施例36	2. 0／4. 0／0. 8／0. 1／0. 0／0. 0	0. 235	93. 1
実施例37	2. 0／4. 0／0. 8／0. 4／0. 0／0. 0	0. 258	94. 0
実施例38	2. 0／4. 0／0. 8／0. 6／0. 0／0. 0	0. 260	94. 0
実施例39	2. 0／4. 0／0. 8／0. 0／0. 1／0. 0	0. 202	94. 1
実施例40	2. 0／4. 0／0. 8／0. 0／0. 6／0. 0	0. 245	93. 8
実施例41	2. 0／4. 0／0. 8／0. 0／0. 0／0. 1	0. 221	93. 5
実施例42	2. 0／4. 0／0. 8／0. 0／0. 0／0. 6	0. 257	94. 2
実施例43	0. 1／0. 1／0. 1／0. 1／0. 0／0. 0	0. 233	92. 8
実施例44	5. 0／6. 5／5. 0／0. 6／0. 0／0. 0	0. 239	94. 2
実施例45	0. 1／0. 1／0. 1／0. 0／0. 1／0. 0	0. 239	93. 0
実施例46	5. 0／6. 5／5. 0／0. 0／0. 6／0. 0	0. 235	93. 5
実施例47	0. 1／0. 1／0. 1／0. 0／0. 0／0. 1	0. 237	93. 3
実施例48	5. 0／6. 5／5. 0／0. 0／0. 0／0. 6	0. 230	94. 2

[0108]When it was 0.1 to 5.0% of the weight of a range, an exceptional difference was not accepted in the increase in the cell thickness in a high-temperature-preservation examination, and the charge-discharge cycle characteristic, but also when it was any, it was good [the addition of PC and VC], so that clearly from Table 3 and 4. From this, the addition of PC and VC was understood that it is preferred to use 0.1 to 5.0% of the weight of the range.
[0109]When it was 0.1 to 6.5% of the weight of a range, an exceptional difference was not accepted in the increase in the cell thickness in a high-temperature-preservation examination, and the charge-discharge cycle characteristic, but the addition of PS was good also when it was any. From this, the addition of PS was understood that it is preferred to use 0.1 to 6.5% of the weight of the range.
[0110]And when it was 0.1 to 0.6% of the weight of a range, an exceptional difference was not accepted in the increase in the cell thickness in a high-temperature-preservation examination, and the charge-discharge cycle characteristic, but also when it was any, it was good [the addition of DPDS, DTDS, and BMPDS]. From this, the addition of DPDS, DTDS, and BMPDS was understood that it is preferred to use 0.1 to 0.6% of the weight of the range.
[0111]When at least one kind chosen from DPDS, DTDS, and BMPDS especially including PC, PS, and VC was added, the charge-discharge cycle characteristic was the best, and it turned out that the generation of gas at the time of high temperature preservation can also be reduced. If the addition total amount of these additive agents is 0.4 to 17.1% of the weight of a range, From an exceptional difference not having been accepted in the increase in the cell thickness in a high-temperature-preservation examination, and the charge-discharge cycle characteristic. The addition total amount at the time of adding at least one kind chosen from DPDS, DTDS, and BMPDS including PC, PS, and VC was understood that it is preferred to use 0.4 to 17.1% of the weight of the range.
[0112]This invention is not limited to the combination of the additive agent of an electrolysis

solution given in the aforementioned Examples 1-48, but replaceable various combination is easily possible for it from the meaning of an invention.

[0113]Although said each example is related with the lithium-polymer battery which used the laminate type battery element, A big effect is acquired when this invention is applied to all the nonaqueous electrolyte secondary batteries that used the lithium containing compound metal oxide for the nonaqueous electrolyte secondary battery, especially the anode and with which it used the fluoro-resin for the negative electrode as at least one binder of graphite and an anode, or a negative electrode.

[0114]

[Effect of the Invention]By using the nonaqueous electrolyte of this invention as mentioned above, the nonaqueous electrolyte secondary battery where the increase in the cell thickness at the time of high temperature preservation was controlled and which was excellent in battery characteristics, such as a charge-discharge cycle characteristic and a conservation characteristic, can be provided.

[Translation done.]